

SCIENCE FOR GLASS PRODUCTION

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THE EFFECT OF EQUILIBRIUM OF HETEROVALENT FORMS OF IRON ON MELTING TEMPERATURE AND GLASS HOMOGENEITY IN INDUSTRIAL PRODUCTION

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The integrated analysis of iron equilibrium in industrial glass-melting float systems of different efficiencies is performed. The close correlation of iron concentration in glass, its melting temperature, and its homogeneity is demonstrated. Reasons for deteriorated glass melt homogeneity in continuous production are analyzed, and practical recommendations are issued.

In any glass one can differentiate its main and impurity compositions. The main composition includes glass-forming agents, modifiers, clarifiers, colorants, opacifiers, and decolorizing agents. The impurity composition is made up of extraneous components that are present in raw materials in small (from 10^{-5} to 1%) quantities and via materials penetrating the glass melt (chlorides, sulfates, *d*- and *f*-elements, etc.).

Construction and container glass is produced using natural materials (sand, chalk, limestone, dolomite, feldspar, kaolin, coal, etc.), waste generated by some industries, and certain chemical reactants (soda, sodium sulfate, saltpeter, selenium). Household and technical glasses have more components introduced via chemical compounds, whereas natural materials are used only in their purified and concentrated forms. Optical and special glass is synthesized predominantly from chemical products: oxides, hydroxides, and salts of purity grades ranging from “technical” to “extra super pure.”

The choice of materials depends on requirements imposed on glass for different purposes and involves the need to minimize to a certain extent the presence of extraneous components that have a negative or unpredictable effect on glass properties.

Iron is the most common impurity. Its content up to 0.5% has little effect on the refractive index, dispersion, CLTE, viscosity, or chemical resistance, but has a perceptible effect on the spectral characteristics and diathermancy of glass [1, 2].

Iron in glass exists in several valence and coordination forms [3]. For practical purposes two valence forms are taken into account: Fe(II) and Fe(III), whose ratio is responsible for the optical properties of glass. Trivalent iron has its absorption band in the ultraviolet spectrum range, whereas bivalent iron — in the infrared spectrum with a maximum at 1000 – 1100 nm. With temperature in a tank furnace ranging from 1500 to 1600°C, the maximum radiation from the flame and the roof is registered in the range near 1500 nm; accordingly, it is evident that the content of bivalent iron in the melt has a direct effect on heat conductivity by radiation and temperature conductivity across the tank depth [3]. To estimate these phenomena, the diathermancy index (DI) has been proposed by the authors in [4], which is numerically equal to

$$DI = 10^{-1} \tau_{1100},$$

where τ_{1100} is the light transmission, %, of a glass sample 10 mm thick for wavelength 1100 nm.

As bivalent iron has the absorption band near 1100 nm, the DI is proportional to the absolute weight content of FeO in glass. The higher the weight content, the lower is the diathermancy index and the lower the diathermancy of glass.

In order to adequately control melting conditions, one should stabilize the DI, which is directly related to the Fe(II) \rightleftharpoons Fe(III) equilibrium position. It may vary within wide limits and depends on the process conditions [3]: fluctuations in the main and impurity material compositions, time-temperature and redox melting conditions, cooling, forming, and annealing; for practical purposes these factors should be considered integrally. This is a complex problem,

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TABLE 1

Glass number	Maximum melting temperature, °C	Homogeneity, °C	Fraction of Fe(II), %	Weight content of iron in glass converted to Fe ₂ O ₃ , %	$K_{\text{bas}} = \frac{R_2O + RO}{SiO_2 + Al_2O_3}$	Batch ROP [3]	Batch from material			Output, tons/day
							new	concentrated	traditional	
1	1500	1.1 – 1.3	30.1	0.118	0.340	6.80	–	–	+	75.0
2	1470	1.1 – 1.3	19.1	0.041	0.328	18.86	–	+	–	75.0
3	1520	1.1 – 1.3	33.5	0.073	0.352	15.48	–	–	+	160.0
4	1560	1.8	38.1	0.180	0.348	13.17	+	–	–	160.0
5	1520	1.1 – 1.3	16.0	0.053	0.351	15.80	–	+	–	160.0
6	1470	1.5 – 2.0	29.5	0.060	0.320	11.72	–	–	+	140.0
7	1510	1.5 – 2.0	37.5	0.071	0.350	9.09	+	–	–	140.0
8	1500	1.5 – 2.0	48.8	0.061	0.351	16.27	–	–	+	140.0
9	1550	1.8 – 2.0	38.9	0.118	No data	15.30	+	–	–	140.0
10	1540	1.8 – 2.0	35.1	0.161	The same	18.90	+	–	–	140.0
11	1510	1.8	32.9	0.122	0.360	11.21	–	–	+	80.0
12	1530	1.9	36.9	0.138	0.390	11.66	+	–	–	80.0
13	1510	1.4	31.7	0.120	No data	13.81	–	–	+	60.4
14	1530	1.8 – 1.9	36.9	0.140	The same	16.25	+	–	–	62.8
15	1515	1.8 – 1.9	31.4	0.130	"	20.10	+	–	–	65.0

* Local dolomite was used instead of Bosnian dolomite.

TABLE 2

Parameter*	Glass based on material		
	concentrated	traditional	local
Visible light transmission			
coefficient, %	90.5	86.0	83.1
Output, tons/day	117.5	109.2	112.5
Batch ROP	17.33	12.55	14.92
Basicity coefficient	0.340	0.345	0.362
Weight content of iron in glass converted to Fe ₂ O ₃ , %	0.047	0.092	0.134
Fraction (weight content) of Fe(II), %	17.6 (0.0058)	34.4 (0.0221)	36.4 (0.0341)
Homogeneity, °C	1.20	1.52	1.83
Maximum melting temperature, °C	1495	1504	1531

* Average values.

TABLE 3

Parameter*	Glass melt basicity with fraction of bivalent iron in glass, %		
	up to 20	20 – 35	over 35
Output, tons/day	117.5	96.7	123.3
Batch ROP	17.33	13.19	14.37
Basicity coefficient	0.340	0.343	0.350
Weight content of iron in glass converted to Fe ₂ O ₃ , %	0.047	0.104	0.124
Fraction (weight content) of Fe(II), %	17.5 (0.0058)	31.5 (0.0229)	38.8 (0.0337)
Homogeneity, °C	1.20	1.52	1.83
Maximum melting temperature, °C	1495	1504	1531

* Average values.

but such approach is the most informative for the production process.

The purpose of the present paper is a complex analysis of the Fe(II) \rightleftharpoons Fe(III) equilibrium in tank furnaces and its effect on melting temperature and glass homogeneity.

Table 1 gives some parameters of industrial glass-melting float systems of capacity 60 – 160 tons/day [5 – 7]. All furnaces are regenerator furnaces with a lateral flame direction, without a bubbling system or electric heating. The batch : cullet ratio in all cases is close to the classical ratio: 70 : 30.

The weight content of Fe₂O₃ was determined by the chemical method, and the content of bivalent iron by the spectrophotometric method; the fraction of Fe(II) was estimated from the expression

$$d_{\text{Fe(II)}} = \frac{\text{Fe(II)}}{\text{Fe}_{\text{tot}}} \times 100\%,$$

where Fe(II) and Fe_{tot} is, respectively, the weight content of total and bivalent iron in glass, converted to metal, %.

The redox potential (ROP) of the batch was calculated according to the data in [3] and the glass basicity coefficient was calculated from the formula

$$K_{\text{bas}} = \frac{R_2O + RO}{SiO_2 + Al_2O_3}.$$

where R₂O, RO, etc. is the molar content, %, of monovalent, bivalent, etc. oxides in glass.

Table 2 compares the process parameters and some characteristics of glass obtained from materials of different degrees of purity regarding iron. Tables 3 ranks all the param-

TABLE 4

Parameter	Number in Table 1					
	2	10	6	12	3	9
Batch ROP	18.86 – 18.90		11.72 – 11.66		15.48 – 15.30	
Weight content of iron in glass converted to Fe ₂ O ₃ , %	0.041	0.161	0.060	0.138	0.073	0.118
Fraction (weight content) of Fe(II), %	19.1 (0.0055)	35.1 (0.0396)	29.5 (0.0124)	36.9 (0.0356)	33.5 (0.0171)	38.9 (0.0321)
Homogeneity, °C	1.1 – 1.3	1.8 – 2.0	1.5 – 2.0	1.9	1.1 – 1.3	1.8 – 2.0
Maximum melting temperature, °C	1470	1540	1470	1530	1520	1550

ters in the order of ascending glass melt basicity that is numerically determined by the bivalent iron fraction indicator [6].

To obtain glass with high transmission of visible light, it is necessary to decrease the iron concentration and to organize the process to shift the Fe(II) \rightleftharpoons Fe(III) equilibrium to the right as much as possible. For this purpose we used concentrated materials and maintained a high ROP of the batch, which made it possible to lower the content of F₂O₃ to 0.0475% and the Fe(II) fraction to 17.6%, and to increase the light transmission coefficient to 90.5%. The diathermancy of such glass melt is so good that even under a minimal plant efficiency of 117.5 tons/day and a relatively low melting temperature, the highest-melting glass of those listed in Table 2 (its basicity coefficient is minimal and equal to 0.340) has the optimum homogeneity of 1.20°C.

The traditional material introduces nearly 2 times more ferrous oxide; furthermore, the decrease in the batch ROP from 17.33 to 12.55 facilitates a double increase in the fraction of Fe(II) and a nearly quadruple increase in the concentration of ferrous oxide. These factors in combination decrease the diathermancy of glass melt so significantly compared with the example described above that even decreasing the plant output to 109.2 tons/day at the same temperature and lowering the glass melt viscosity determined by the glass melt basicity coefficient to 0.345 did not improve the glass homogeneity. The achieved homogeneity value is 1.5°C.

When dolomite from Bosnia was replaced by dolomite from local deposits, the weight content of iron in glass grew by 50% and reached 0.134%. A decrease in glass melt viscosity ($K_{\text{bas}} = 0.39$), an increase in the batch ROP to 14.92, and raising the melting temperature to 1534°C did not yield positive results. The fraction of ferrous oxide and its mass content grew to 36.4 and 0.0341%, respectively, and the homogeneity deteriorated to 1.85°C.

The increase in glass melt basicity contributing to a decreased melt viscosity together with the increase in total iron content raise the fraction and mass content of ferrous oxide, increase the melting temperature, and degrade the glass melt homogeneity. An increase in the batch ROP from 13.19 to 14.37 did not shift the Fe(II) \rightleftharpoons Fe(III) equilibrium to the right, since the opposite effect of the melting temperature dominated.

TABLE 5

Parameter	Number in Table 1		
	1	13	9
Fraction (weight content) of Fe(II), %	30.1	31.7	38.9
Homogeneity, °C 1.1 – 1.3	1.4	1.8 – 2.0	
Maximum melting temperature, °C	1500	1510	1550

TABLE 6

Parameter	Number in Table 1			
	1	3	9	12
Homogeneity, °C	1.1 – 1.3		1.9	
Weight content of iron in glass converted to Fe ₂ O ₃ , %	0.118	0.073	0.118	0.138
Fraction (weight content) of Fe(II), %	30.1 (0.0242)	33.5 (0.0171)	38.9 (0.0321)	36.9 (0.0356)
Basicity coefficient	0.340	0.352	No data	
Batch ROP	6.80	15.48	15.30	11.66
Maximum melting temperature, °C	1500	1520	1550	1530
Output, tons/day	75	160	140	80

Table 4 compares glasses from Table 1 with close batch ROP values, and Table 5 compares glasses with an equal content of total iron converted to Fe₂O₃ (0.118 – 0.120%).

It can be seen from the data in Table 4 that in all considered cases, the increasing weight content of total and bivalent iron is accompanied by increased melting temperature and deteriorated glass homogeneity. The bivalent iron fraction grows as well. It is known that the Fe(II) \rightleftharpoons Fe(III) equilibrium shifts to the right as the iron concentration decreases and shifts to the left with increasing melting temperature [8, 9]. Apparently, the influence of melting temperature prevails.

Under a steady iron oxide content equal to 0.118 – 0.120%, an increased fraction and weight content of bivalent iron caused by different reasons is accompanied by consistent deterioration of glass homogeneity, and even raising the melting temperature does not improve this parameter.

Table 6 compares the process parameters with different melt output that yield glass of identical homogeneity, and Ta-

TABLE 7

Parameter	Number in Table 1			
	7	11	2	6
Homogeneity, °C	1.75	1.80	1.75	1.20
Weight content of iron in glass converted to Fe ₂ O ₃ , %	0.071	0.122	0.060	0.041
Fraction (weight content) of Fe(II), %	37.5	32.9	29.5	19.1
	(0.0186)	(0.0280)	(0.0123)	(0.0055)
Basicity coefficient	0.350	0.360	0.320	0.328
Batch ROP	9.09	11.21	11.72	18.86
Maximum melting temperature, °C	1510	1510	1470	1470
Output, tons/day	140	80	140	75

TABLE 8

Parameter	Number in Table 1			
	3	4	7	5
Batch ROP	15.45	13.17	9.09	15.80
Weight content of iron in glass converted to Fe ₂ O ₃ , %	0.073	0.180	0.071	0.053
Fraction (weight content) of Fe(II), %	33.5	38.1	37.5	16.0
	(0.0171)	(0.0480)	(0.0186)	(0.0060)
Homogeneity, °C	1.20	1.80	1.75	1.80
Maximum melting temperature, °C	1520	1560	1510	1520
Output, tons/day	160	160	140	160

ble 7 compares the homogeneity of glass melt melted at the same temperature.

It can be seen from Table 6 that as the output grows approximately 2 times, to preserve the homogeneity at the same level, the content of iron has to be decreased by using concentrated materials or including magnetic separation in the batch hopper – glass-melting furnace technological chain. To improve the glass melt diathermancy (related to the concentration of bivalent iron), the ROP of the batch is increased. In general, to keep the homogeneity at the same level, the melting temperature is raised by about 20°C.

Analysis of glasses 7 and 11 (Table 7) indicates that using concentrated materials with a low iron content in large furnaces even under higher glass viscosity and a decreased batch ROP provides comparable or better homogeneity than that of a less viscous glass melted from ordinary materials in a lower-output furnace. The use of material contaminated with iron in combination with increase infusibility of glass and a decreased batch ROP sharply degrades the homogeneity of glass (Table 7, glasses 2 and 6).

The effect of technological parameters on iron equilibrium and homogeneity of glasses of an identical composition is shown in Table 8. It can be seen that the effect of glass

composition on its properties and glass melting parameters is excluded: the basicity coefficient is equal to 0.350 – 0.351.

To simplify the analysis, all parameters considered in Table 8 are ranked in the order of increasing values.

Batch ROP 7 → 4 → 3 → 5
 Weight content of:
 iron converted to Fe₂O₃, % 5 → 7 → 3 → 4
 Fe(II) 5 → 3 → 7 → 4
 Fraction of Fe(II), % 5 → 3 → 7 → 4
 Homogeneity 3 → 5 → 7 → 4
 Maximum melting temperature. 7 → 5 → 3 → 4

The concentration of iron in glass 5 is minimal; therefore, considering also the high ROP of the batch we have obtained glass with optimum homogeneity equal to 1.2°C.

Glass 7 has a higher concentration of total iron; however, the minimal ROP of the batch has led to a perceptible increase in the absolute concentration and fraction of bivalent iron. As a consequence, the homogeneity has deteriorated to 1.75°C. This glass also has the lowest melting temperature considered, which is inadmissible for glass with low diathermancy.

Glass 3 has an iron content comparable to glass 7, whereas 1.5 times increase of the ROP shifts the Fe(II) ⇌ Fe(III) equilibrium to the right and improves the diathermancy. The homogeneity of this glass is 1.2°C.

Finally, the content of iron oxide is maximum in glass 4. The low ROP of the batch has shifted the equilibrium toward the ferrous oxide, accordingly, the concentration and fraction of Fe(II) have reached maximum values, consequently, the diathermancy of the melt has deteriorated and even at a melting temperatures of 1560°C the homogeneity of this glass is 1.8°C.

The integrated analysis of operation of glass-melting furnaces suggests the following:

- maximum effect in lowering the mass content and fraction of bivalent iron is achieved by using concentrated materials in combination with an increased ROP of the batch; in this case even a low melting temperature yields glass with good homogeneity;
- an increased iron concentration is accompanied by deteriorated glass homogeneity and requires raising the ROP of the batch and the melting temperature;
- when the material has an increased iron content, even decreasing the melt viscosity and raising the batch ROP and melting temperature cannot always guarantee glass of high homogeneity;
- in industrial conditions the melting temperature has a more significant effect on Fe(II) ⇌ Fe(III) equilibrium than changing the concentration of iron oxide.

REFERENCES

1. *Physicochemical Principles of Optical Glass Production* [in Russian], Khimiya, Leningrad (1976).
2. Yu. A. Guloyan, "Solidification of glass in molding," *Steklo Keram.*, No. 11, 3 – 7 (2004).

3. Type of defects in glass production. Stroiizdat, Moscow (1986).
4. Yu. A. Guloyan, *Efficiency of Technological Processes in Production of Glass Products* [in Russian], Legkaya Prom-st', Moscow (1982).
5. V. I. Kiyan, E. K. Polokhlivets, P. A. Krivoruchko, and A. B. Atkarskaya, "Redox potential of glass melt in a continuous technological process," *Steklo Keram.*, No. 11, 10 – 12 (1999).
6. V. I. Kiyan and A. B. Atkarskaya, "Experience in applying basicity indicators to estimate the redox potential of glass melt in continuous production," *Steklo Keram.*, No. 3, 9 – 13 (2002).
7. V. I. Kiyan, P. A. Krivoruchko, A. B. Atkarskaya, "Inner reserves for increasing efficiency of glass-melting furnaces," *Steklo Keram.*, No. 8, 8 – 11 (1999).
8. A. G. Dunn and K. J. Beales, "Near Infrared Optical Absorption of Iron (II) in Sodium-Borosilicate Glasses," *Phys. Chem. Glasses*, **19**(1), 1 – 4 (1978).
9. A. Paul and R. W. Douglas, "Ferrous-Ferric Equilibrium in Binary Alkali Silicate Glasses," *Phys. Chem. Glasses*, **6**(6), 207 – 211 (1965).